temperature 23 °C, 16 or 32K data points, sweep width 4 kHz giving a digitization accuracy of 0.25 or 0.5 Hz/point, pulse width 7 Ms, aquisition time 1 or 2 s, and ca. 80 accumulations. Probe temperatures were controlled with the spectrometer variable-temperature control unit, and a 15 min equilibration time was allowed between each spectrum. Saturation transfer experiments were performed by narrowing down the sweep width of, e.g., the Nicolet NT-360 instrument to $\pm$–2000 Hz and then obtaining a 32K spectrum with resolution of 0.3 Hz. The decoupler was set to a chosen frequency at the downfield end of the spectrum (reference) and the second frequency was set to saturate the peak of interest in the BChlide-*d* [Et, Et] dimer. The pulse width was set to zero (hetero mode) and the output level was 28 dB. A decay of about 4 times the aquisition time preceded a 45° pulse (6.00 μs) which was short enought to allow detection of the saturation transfer effects while still observing NOE effects. The decoupler was off during the acquisition time. Fourier transformation followed by subtraction of the saturation transfer spectrum from the reference spectrum gave the difference spectra shown in Figure 1.

Trideuteriomethyl 10,10-Dideuteriobacteriochlorophyllide *d* [Et, Et] (2). A solution of methyl bacteriopheophorbide *d* [Et, Et][35] (33.8 mg) in 3% D_2SO_4/CD_3OD (5 mL) was stirred overnight under a nitrogen atmosphere. Dichloromethane and aqueous sodium acetate were added, and the organic phase was rinsed with water, dried (Na_2SO_4), and evaporated to give a green residue that was chromatographed on a Harrison Research chromatotron, silica gel plate, elution with 3% tetrahydrofuran in dichloromethane. The eluates containing the major green band were evaporated to give a green residue. NMR, (Nicolet NT-500, $CDCl_3$), 9.53 (s, 1 H, α-meso-H), 9.43 (s, 1 H, β-meso-H), 8.45 (s, 1 H, δ-meso-H), 6.26 (q, 2a-H), 5.13 (ABq, 10-CH_2, >95% deuterated), 4.41 (m, 1 H, 8-H), 4.19 (m, 1 H, 7-H), 4.02 (ABX_3, 2 H, 5a-CH_2), 3.62 (s, OMe, >95% deuterated), 3.33 (s, 3 H, 1-Me), 3.19 (s, 3 H, 3-Me), 2.50–2.63 and 2.20–2.27 (each m, 5 H, 7a,b-CH_2CH_2 and 2a-OH), 2.06 (d, $J = 6.6$ Hz, 3 H, 2b-Me), 1.92 (t, $J = 7.5$ Hz, 3 H, 5b-Me), 1.75 (d, $J = 7.2$ Hz, 3 H, (-Me), 1.67 (t, $J = 7.6$ Hz, 3 H, 4b-Me), 0.28, −1.84 ppm (each br s, each 1 H, NH). Magnesium was inserted into this sample with the Eschenmoser BHT procedure[34] to give 16.57 mg (47%) of the required d_5-deuterated BChlide-*d*.

Methyl 5a,5a,7b,7b,10,10-Hexadeuteriobacteriochlorophyllide *d* [Et, Et] (5). A solution of methyl bacteriopheophorbide *d* [Et, Et] (23.9 mg) in CH_3OD (5 mL) containing sodium hydroxide (150 mg) was refluxed for 3 h under a nitrogen atomosphere. The solution was cooled by using an ice/water bath before addition of 25% aqueous acetic acid to pH 7. The mixture was partitioned between dichloromethane and water and washed with aqueous sodium bicarbonate, and the organic phase was dried (Na_2SO_4) and evaporated to give a residue that was redissolved in 3% H_2SO_4 in methanol and stirred for 3 h at room temperature. Dichloromethane and aqueous sodium acetate were added and the organic phase was rinsed with water, dried (Na_2SO_4), and evaporated to give a green residue that was chromatographed on a silica gel preparative plate (elution with 3% tetrahydrofuran in dichloromethane). Extraction of the appropriate band followed by evaporation gave the hexadeuterated methyl bacteriopheophorbide *d* (1.61 mg; 6.8%). NMR, (Nicolet NT-500, $CDCl_3$) 9.53 (s, 1 H, α-meso-H), 9.43 (s, 1 H, β-meso-H), 8.45 (s, 1 H, δ-meso-H), 6.26 (q, 2a-H), 5.13 (ABq, 10-CH_2, ca. 70% deuterated), 4.41 (m, 1 H, 8-H), 4.19 (m, 1 H, 7-H), 4.02 (ABX_3, 5-CH_2, >95% deuterated), 3.62 (s, 3 H, OMe), 3.33 (s, 3 H, 1-Me), 3.19 (s, 3 H, 3-Me), 2.65 and 2.29 (each m, each 1 H, 7a-CH_2CD_2), 2.59 (s, 1 H, 2a-OH), 2.06 (d, $J = 6.6$ Hz, 3 H, 2b-Me), 1.92 (s, 3 H, 5b-CD_2CH_3, 1.75 (d, $J = 7.2$ Hz, 3 H, −Me), 1.67 (t, $J = 7.6$ Hz, 3H, 4b-Me), 0.28, −1.84 ppm (each br s, each 1 H, NH). Magnesium was inserted into this sample by using the Eschenmoser BHT procedure[34] to afford the required d_6-deuterated BChlide-*d*.

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Gas-Phase Reactions of V$^+$ and VO$^+$ with Hydrocarbons Using Fourier Transform Mass Spectrometry

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Abstract: The reactions of V$^+$ and VO$^+$ with small alkanes are reported. V$^+$ reacts with hydrocarbons primarily by inducing dehydrogenation, showing a marked preference for C–H bond insertion, giving rise to products corresponding to C–C bond insertion only when C–H reaction pathways are blocked. Unlike later transition metals, V$^+$ will undergo secondary reactions with most alkanes, producing complexes having more than one hydrocarbon ligand. The presence of oxygen as a ligand on V$^+$ has surprisingly little effect on reactivity and only influences reactions when coordinative saturation becomes a factor. In contrast to FeO$^+$, the oxide ligand is not observed to participate in the reactions, due undoubtedly to the strong V$^+$–O bond.

The study of the chemistry of gas-phase metal ions often begins with an examination of their interactions with hydrocarbons, due to the importance of hydrocarbons in organometallic chemistry and catalysis and also to the ubiquitous presence of a hydrocarbon chain in other organic molecules of interest.[1] Most of the work to date has been concentrated on the groups 8–10 metal cations, Fe$^+$, Co$^+$, and Ni$^+$ due to their importance in catalysis,[2] although preliminary studies have also been reported for a variety of other gas-phase metal ions.[1b,3] This paper is a continuation of our work in this area and reports the reactivity of the early first-row transition-metal ion, V$^+$, with hydrocarbons. Since oxide chemistry is prominent in the solution chemistry of vanadium, and since formation of VO$^+$ is observed in the gas-phase reactions of V$^+$ with many oxygen-containing species, the chemistry of VO$^+$ is also reported. In a similar study comparing the reactions of Fe$^+$

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(1) (a) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332. (b) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565. (c) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963.

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(3) (a) Burnier, R. C.; Carlin, T. J.; Reents, W. D., Jr.; Cody, R. B.; Lengel, R. K.; Freiser, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 7127. (b) Weil, D. A.; Wilkins, C. L. *J. Am. Chem. Soc.* **1985**, *107*, 7316. (c) Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944. (d) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4065. (e) Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403. (f) Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 8117.

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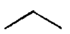
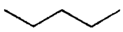
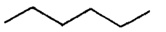
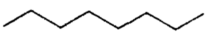
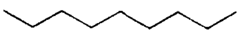
Table I. Primary and Secondary Reactions of V^+ with Linear Alkanes

	primary reactions		secondary reactions	
alkane	neutral(s) lost	relative %	neutral(s) lost	relative %
CH_4	no reaction			
C_2H_6	no reaction			
	H_2	100	H_2	50
			$2H_2$	50
	H_2	13	[a]	
	$2H_2$	87	H_2	92
			$2H_2$	8
	$2H_2$	100	$2H_2$	100
	$2H_2$	54	$3H_2$	61
			$2H_2$	39
	H_2, C_2H_6	23	$2H_2$	77
			$2H_2$, CH_4	16
			H_2, CH_4	7
	$3H_2$	12	[a]	
	$4H_2$	11	[a]	
	$2H_2$, CH_4	32	$2H_2$	100
	$3H_2$	28	H_2, CH_4	100
	$2H_2$	26	$2H_2$, CH_4	100
	H_2, C_2H_6	5	$3H_2$	67
			$2H_2$	33
	H_2, C_3H_8	7	$2H_2$	100
	$3H_2$, CH_4	2	[a]	
	$3H_2$	100	no reaction	
	$3H_2$	100	no reaction	

[a] The intensity of the primary product ion was insufficient to allow further study.

and FeO^+,[4] the presence of the oxygen ligand was found to greatly increase the reactivity of the ion. For vanadium, however, the presence of oxygen does not greatly affect the chemistry, which can be attributed to the greater bond energy of vanadium ion to oxygen. Recent reports by Aristov and Armentrout[3d] giving various thermochemical properties of gas-phase V^+ complexes have added to the amount of information available from our results.

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer, which has been previously described in detail[5] and is equipped with a 5.2 cm cubic trapping cell situated between the poles of a Varian 15 in. electromagnet maintained at 0.9 T. The cell has a $^1/_4$ in. hole in one of the transmitter plates permitting irradiation of the interior with various light sources. V^+ was generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto a thin high purity vanadium foil which was supported on the opposite transmitter plate. VO^+ was generated by trapping V^+ in the presence of O_2 which was admitted to the cell through a General Valve Corp. Series 9 pulsed solenoid valve. Details of the laser ionization[3c,6] and pulsed valve[7] experiments are described elsewhere. Pulsing in the O_2 allows the system to be maintained at a lower pressure during the majority of the reaction sequence which enables ions to be trapped more efficiently and also eliminates any further reaction with O_2.

The product ion distributions are reproducible to within ±10% absolute. Product distributions of secondary reactions were determined by using swept double resonance ejection techniques to isolate the ions of interest.[8] These ions were allowed to react and the products subsequently detected.

Details of the CID experiments have been discussed previously.[2b,9] The collision energy of the ions can be varied, typically between 0 and 100 eV, from which plots of CID product ion intensities vs. collision energy can be produced. The distribution of the kinetic energies is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.[10] Simple metal ion complexes can be assigned structures via CID unambiguously. Complexes containing ligands possessing five or more carbon atoms, however, cannot always be assigned definitive structures, since these species may undergo facile rearrangements which may yield CID spectra that are not very diagnostic. Thus, while CID spectra of many product ions were obtained, many of the structures are assigned as "reasonable" as opposed to proven.

In the typical FTMS metal cation experiment, metal ions are created and trapped in the presence of the hydrocarbon of interest. After a suitable interaction time, the mass spectrum is obtained, detecting all ions present in the cell. Laser ionization can produce metal ions that are kinetically or electronically excited.[11] In order to minimize these effects, two sets of data were produced under conditions designed to remove excess kinetic energy from the V^+ ions. The first method involved admitting a relatively high pressure argon pulse to the cell (~10^{-5} torr) followed by a brief interaction time (~200 ms) for the trapped V^+ ions to be collisionally dampened. After this deactivation step, V^+ was isolated and allowed to react with the hydrocarbon of interest which was present at a static background pressure. In the second method, the V^+ ions were allowed to interact with the hydrocarbon present. After a suitable interaction time (~500 ms), all ions but V^+ were ejected from the cell, and reaction products were observed after a reaction interval. The product distributions resulting from either method were identical within experimental error. In addition, for the majority of the reactions studied, there was no significant difference between the product distributions arising from cooled or uncooled V^+. Just one example of an excited-state reaction is discussed, $VC_3H_5^+$ from propane, and only results from cooled ions are tabulated.

Chemicals were obtained in high purity from commercial sources and used as suppled except for multiple freeze-pump-thaw cycles to remove noncondensible gases. Sample pressures were measured with a Bayard-Alpert-type ionization gauge and were typically on the order of 1×10^{-7} torr. Argon was used as a collision gas at a total pressure (sample plus argon) of approximately 5×10^{-6} torr.

Results and Discussion

Reactions of V^+ with Alkanes. In general, the reactions of V^+ with alkanes are similar to those previously reported for Ti^+[1b]

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(5) (a) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *41*, 199. (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

(6) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

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(8) (a) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413. (b) Marshall, A. G.; Comisarow, M. B.; Parisod, G. *J. Chem. Phys.* **1979**, *71*, 4434. (c) Parisod, G.; Comisarow, M. B. *Adv. Mass Spectrom.* **1980**, *8*, 212.

(9) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736.

(10) Huntress, W. T.; Mosesman, M. M.; Elleman, D. D. *J. Chem. Phys.* **1971**, *54*, 843.

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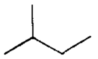
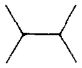
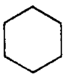
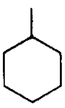
Table II. Primary and Secondary Reactions of V^+ with Branched Alkanes

	primary reactions		secondary reactions	
alkane	neutral(s) lost	relative %	neutral(s) lost	relative %
	H_2	98	$2H_2$	100
	$2H_2$	2	*a*	
	$2H_2$	100	H_2	70
			$2H_2$	30
	CH_4	100	CH_4, H_2	74
			CH_4, $2H_2$	13
			$2H_2$	8
			H_2	5
	$2H_2$	89	$2H_2$	90
			H_2	10
	H_2, CH_4	6	*a*	
	C_3H_8	5	*a*	
	H_2, CH_4	43	C_2H_6	37
			CH_4, H_2	33
			$2H_2$	11
			H_2	10
			C_2H_6, H_2	9
	H_2	22	*a*	
	C_2H_6	19	CH_4, H_2	50
			C_2H_6	31
			C_2H_6, H_2	19
	$2H_2$	16	*a*	
	$2H_2$	38	no reaction	
	$3H_2$	36	no reaction	
	C_4H_{10}	26	C_4H_8, $2H_2$	58[b]
			C_4H_8, H_2	42

[a] The intensity of the primary product ion was insufficient to allow further study. [b] $VC_4H_8^+$ reacts to generate the initial two products listed.

Table III. Primary and Secondary Reactions of V^+ with Cyclic Alkanes

	primary reactions		secondary reactions	
alkane	neutral(s) lost	relative %	neutral(s) lost	relative %
	H_2	100	$2H_2$	56
			C_2H_4	27
			H_2	17
	C_2H_4	90	C_2H_6	53
			C_2H_4	34
			H_2	7
			$3H_2$	6
	H_2	10	$2H_2$	74
			C_2H_6, H_2	17
			CH_4, H_2	9
	$2H_2$	100	$3H_2$	100
	$3H_2$	74	$2H_2$	76
			$3H_2$	24
	$2H_2$	26	$3H_2$	78
			$4H_2$	22
	$3H_2$	63	$3H_2$	54
			$2H_2$	46
	CH_4, $2H_2$	37	$3H_2$	61
			$2H_2$	39

and Rh^+.[3c] Most of the products result from single or multiple dehydrogenations, although alkane or alkene losses predominate for some branched alkanes. Tables I–III list the primary and major secondary reaction products observed for the alkanes studied. In all cases except for cyclopropane, the secondary products were not observed to undergo further reaction. This is not surprising, since these product ions are highly coordinatively saturated. The reactions observed are rationalized mainly by initial carbon–hydrogen bond insertion, but formation of some of the products suggests that carbon–carbon bond insertion can also occur for species with weak carbon–carbon bonds.

Linear Alkanes. Propane is the smallest hydrocarbon which reacts with V^+, producing $VC_3H_6^+$, reaction 1. This reaction is

$$V^+ + C_3H_8 \rightarrow VC_3H_6^+ + H_2 \qquad (1)$$

considerably slower than those of V^+ with larger hydrocarbons, which may be due to a weak $D°(V^+–C_3H_6)$ which renders the reaction nearly thermoneutral. This, in turn, suggests a value for $D°(V^+–C_3H_6)$ of ca. 30 kcal mol^{-1},[12] which compares reasonably well to $D°(V^+–C_2H_4) = 33$ kcal mol^{-1} reported by Aristov and Armentrout.[3d] This product reacts further with propane to produce, by loss of H_2 and $2H_2$, complexes corresponding to $VC_6H_{12}^+$ and $VC_6H_{10}^+$.

In addition to the $VC_3H_6^+$ complex, $VC_3H_5^+$ is formed if the V^+ is formed with excess kinetic energy, reaction 2. This product is not observed from collisionally cooled V^+. The assumption

$$V^{+*} + C_3H_8 \rightarrow VC_3H_5^+ + H_2 + H \qquad (2)$$

that this reaction is endothermic yields $D°(V^+–C_3H_5) < 118$ kcal mol^{-1}. A secondary reaction of the V^+–allyl was observed, forming $VC_6H_{11}^+$ by loss of H_2. Presumably, this reaction does not require that the $VC_3H_5^+$ complex have excess energy.

Chemistry analogous to $VC_3H_6^+$ was observed for $RhC_3H_6^+$.[3c] In that case, the reaction was proposed as occurring through an allyl–hydride structure. Furthermore, the $RhC_3H_6^+$ ion was observed to undergo five H/D exchanges in the presence of excess D_2. In an earlier ICR study by Beauchamp et al.,[13] $CpRhC_3H_5^+$ generated via reaction 3 was observed to undergo only four H/D

$$CpRhD^+ + C_3H_8 \rightarrow CpRhC_3H_5^+ + HD, H_2 \qquad (3)$$

exchanges indicating that the allyl hydrogen is preserved. In the present study, neither $VC_3H_5^+$ nor $VC_3H_6^+$ was observed to undergo H/D exchange with D_2. Lack of H/D exchange with D_2 cannot, however, be taken as evidence against a hydride structure since FeH^+ is not observed to exchange with D_2.[14] One possible explanation for failure to observe H/D exchange is D_2 simply does not oxidatively add to the metal. Alternatively, if a propene structure is favored over an allyl–hydride structure, either there is a barrier to exchange or elimination of D_2 is faster than scrambling. It should be noted that while $RhC_3H_6^+$ does undergo H/D exchange with D_2, analogous Fe, Co, and Ni species do not undergo exchange.[3c,15] C_2D_4 has been shown to be a somewhat more efficient deuterating reagent than D_2[15] and, when exposed to this reagent, $VC_3H_6^+$ does undergo five H/D exchanges. Presumably, coordination of the C_2D_4 imparts enough energy to the complex (ca. 30 kcal mol^{-1}) to allow H/D exchange (reaction 4). $VC_3H_5^+$, on the other hand, does not undergo H/D exchange

$$VC_3H_{6-n}D_n^+ + C_2D_4 \rightarrow VC_3H_{5-n}D_{n+1}^+ + C_2D_3H \ (n = 0–4) \qquad (4)$$

with either reagent. Neither of the secondary products, $VC_6H_{10}^+$ nor $VC_6H_{12}^+$, undergoes H/D exchange with either reagent. These ions are probably either locked into the bis(allyl) or the bis(propene) structure, respectively, or there is sufficient steric crowding to prevent initial coordination of C_2D_4.

The bis-olefin product, $VC_6H_{12}^+$, undergoes collisional activation readily to form the bis-allyl ion, $VC_6H_{10}^+$. CID of $VC_6H_{10}^+$ gives four products, reactions 5–8, with reactions 5 and 6 dominating over the range of kinetic energies studied. Reaction 5 probably

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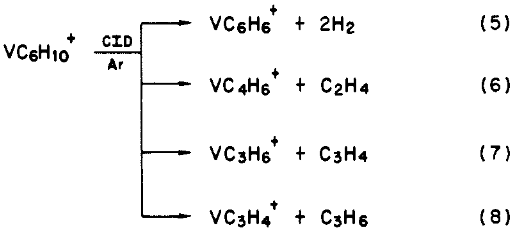
[12] Calculated with use of values in the following: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1.

[13] Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967.

[14] Carlin, T. J.; Sallans, L.; Cassady, C. J.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6320.

[15] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

involves a dehydrocyclization process, in analogy to the catalytic aromatization of linear alkanes which is a well-known reaction in the hydrocarbon reforming process[16] and has been observed for a number of other gas-phase metal-ion systems.[17] The $VC_4H_6^+$ product is presumably a V^+–butadiene species.



$$VC_6H_{10}^+ \xrightarrow[Ar]{CID} VC_6H_6^+ + 2H_2 \quad (5)$$
$$\phantom{VC_6H_{10}^+ \xrightarrow[Ar]{CID}} VC_4H_6^+ + C_2H_4 \quad (6)$$
$$\phantom{VC_6H_{10}^+ \xrightarrow[Ar]{CID}} VC_3H_6^+ + C_3H_4 \quad (7)$$
$$\phantom{VC_6H_{10}^+ \xrightarrow[Ar]{CID}} VC_3H_4^+ + C_3H_6 \quad (8)$$

These results are interesting in contrast to those obtained with Fe^+ and Co^+.[18] For these metals, CID of the bis(propene) complexes at low kinetic energies yields simple cleavage, regenerating the M^+–propene complex, and at higher energies the bare metal ion is regenerated. The bis(allyl) complexes of Fe^+ and Co^+, however, undergo the same four reactions as the V^+ complex.

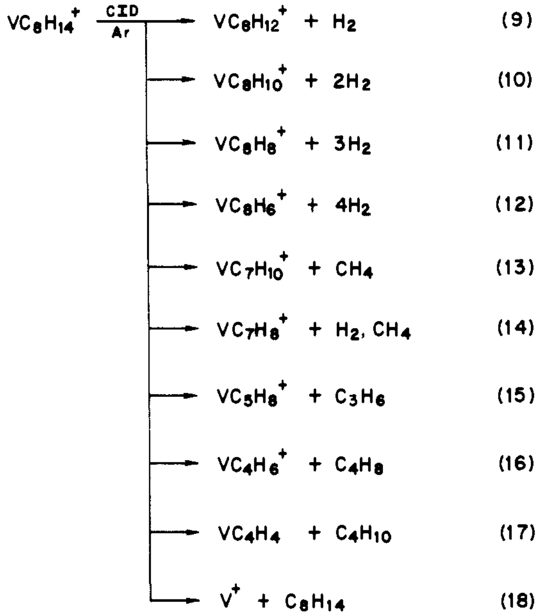
The V^+ ion reacts with butane and pentane by eliminating two molecules of H_2 to form alkadiene complexes. Assuming exothermic formation of $VC_4H_6^+$ from V^+ and butane implies $D°(V^+–C_4H_6) \geq 56$ kcal mol^{-1}. This value compares favorably with $D°(Co^+$–butadiene$) = 45–60$ kcal mol^{-1} as reported earlier.[19,20] Interestingly, formation of a single dehydrogenation product is also seen with butane but is not observed with pentane. This trend is followed in the secondary reactions of the products; $VC_4H_6^+$ reacts with butane to produce both single and double dehydrogenation products, while $VC_5H_8^+$ reacts with pentane to produce only the double dehydrogenation product.

The single dehydrogenation product of V^+ with butane, $VC_4H_8^+$, readily eliminates one molecule of H_2 upon collisional activation, producing the V^+–butadiene complex. At higher energies, a small amount of $VC_4H_4^+$ is observed and V^+ is regenerated. These results suggest that $VC_4H_8^+$ has a V^+–butene structure[2b] and must be formed with little excess internal energy in order to be observed.

In addition to multiple dehydrogenations, the combined loss of H_2 and small alkanes is a major reaction pathway for hexane and heptane. These results are not inconsistent with initial carbon–hydrogen bond insertion which, followed by H_2 elimination, yields a vibrationally excited metal–alkene species which then dissociates by eliminating various alkanes.[2b,4]

For octane and nonane, however, formation of a triene by loss of $3H_2$ is the only major product, and these products are unreactive with the alkane. Apparently, since it is possible for each of these molecules to form an internal, conjugated triene without abstraction of the more strongly bound terminal hydrogens, triene formation becomes the most energetically favorable pathway. CID of either of the triene products results predominantly in formation of a $VC_5H_5^+$ species, which, when further activated, forms V^+, consistent with formation of V^+–c-C_5H_5. A similar dehydrocyclization has been observed for CoCp$^+$ complexes.[21]

Branched Alkanes. 2-Methylpropane reacts with V^+ to eliminate H_2, forming a V^+–isobutene complex as the major primary product. A small (~2%) amount of $VC_4H_6^+$ is also formed. Collisional activation of the $VC_4H_8^+$ complex gives, at low energy, some formation of $VC_4H_6^+$ and direct cleavage to regenerate V^+. At higher energies only the latter process is observed. The small amount of the $VC_4H_6^+$ product formed suggests that formation of a V^+–trimethylenemethane or metal-mediated rearrangement to V^+–butadiene are not favorable processes, in analogy to earlier studies.[2f,9] Thus, the two isomeric species V^+–butene and V^+–isobutene are stable and readily distinguishable. Both the $VC_4H_8^+$ and $VC_4H_6^+$ products react with a second molecule of 2-methylbutane to produce a $VC_8H_{14}^+$ complex, which presumably has a bis(methallyl) structure. CID of this ion yields, at low energies, ions formed from extensive dehydrogenation (reactions 9–12) with, presumably, extensive rearrangement. This is exemplified by formation of $VC_8H_6^+$, which corresponds to successive losses of $4H_2$ from the parent ion. At higher energies, cleavage products are seen, reactions 13–18. For the analogous Co^+ species, dehydrogenation is not as extensive.[18]



$$VC_8H_{14}^+ \xrightarrow[Ar]{CID} VC_8H_{12}^+ + H_2 \quad (9)$$
$$VC_8H_{10}^+ + 2H_2 \quad (10)$$
$$VC_8H_8^+ + 3H_2 \quad (11)$$
$$VC_8H_6^+ + 4H_2 \quad (12)$$
$$VC_7H_{10}^+ + CH_4 \quad (13)$$
$$VC_7H_8^+ + H_2, CH_4 \quad (14)$$
$$VC_5H_8^+ + C_3H_6 \quad (15)$$
$$VC_4H_6^+ + C_4H_8 \quad (16)$$
$$VC_4H_4 + C_4H_{10} \quad (17)$$
$$V^+ + C_8H_{14} \quad (18)$$

The observed neutral losses produced from the primary and secondary reactions of V^+ with 2-methylbutane correspond very well with those observed for butane, with the only significant difference being a slight variation in the secondary product ion ratios. These data support the hypothesis that V^+ prefers C–H insertion over C–C insertion since a greater difference in product ions formed would be expected when changing from the unsubstituted butane to 2-methylbutane.

2,2-Dimethylpropane is often used as a test of C–H bond insertion mechanisms, since, following initial C–H bond insertion, there are no β-hydrogens available for reductive elimination of an H_2 molecule. V^+ reacts with this species at a rate approximately ten times slower than with the other hydrocarbons discussed previously, to produce V^+–isobutene by CH_4 loss. The slowness of this reaction provides further evidence for the tendency of V^+ to insert into C–H bonds, since initial insertion into a C–C bond would permit a facile β-hydrogen shift to eliminate methane, whereas insertion into a C–H bond requires a β-methyl shift for methane loss. A C–C bond insertion would require that $D°(CH_3–t\text{-}C_4H_9) = 84.1 \pm 0.1$ kcal/mol[23] $< D°(V^+–CH_3) + D°(CH_3V^+–t\text{-}C_4H_9)$ or $D°(CH_3–t\text{-}C_4H_9) = 84.1 \pm 0.1$ kcal/mol $< D°(V^+–t\text{-}C_4H_9) + D°(t\text{-}C_4H_9V^+–CH_3)$.

Armentrout has reported that $D°(V^+–CH_3) = 54 \pm 4$ kcal mol^{-1}, and assuming that a second alkyl group binds with comparable energy,[3d] this seems to be an achievable requirement. Therefore, kinetic rather than thermodynamic factors are apparently involved.

The vanadium cation reacts with 2,3-dimethylbutane in a manner resembling that of 2-methylbutane, producing the substituted butadiene as the major product, but also producing some products that correspond to alkane loss. In contrast, 2,2-dimethylbutane is unable to form a substituted butadiene without

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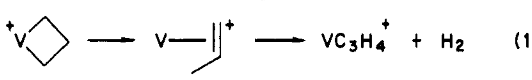
considerable rearrangement of the carbon skeleton, and this product is seen only in relatively small yield. The major products correspond to alkane losses or a single dehydrogenation, as would be expected.

The highly branched alkane 2,2,3,3-tetramethylbutane possesses a weak central C–C bond (71.1 ± 1 kcal mol^{-1})[23] but no hydrogens β to initial C–H bond insertion sites. Nonetheless, two of the three primary products observed are the result of multiple dehydrogenations, while the third probably results from insertion into the central C–C bond, followed by elimination of C_4H_{10} to form a $VC_4H_8^+$ ion, again shown to be a V^+–isobutene species.

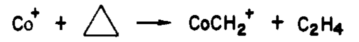
Cyclic Alkanes. V^+ reacts with cyclic alkanes primarily by inducing dehydrogenation, with multiple dehydrogenations observed for rings containing five or more carbons. The secondary reactions also result in single or multiple dehydrogenations.

Cyclopropane and V^+ react to give a single primary reaction product by H_2 loss. Although this reaction is relatively slow, the product formed is quite reactive and the secondary products are extensive. Presumably, reaction occurs by insertion into the weak C–C bond, forming a metallacyclobutane ion, I, which rearranges to a V^+–propene complex,[24] followed by elimination of H_2, reaction 19. In support of this mechanism, V^+ is observed to also react with propene to produce a $VC_3H_4^+$ species. The products observed for $Rh^{+\,7a}$ and $Ti^{+\,1b}$ with cyclopropane are more varied than for V^+, but in each case the H_2 loss product is the predominant ion observed, while no reactions were observed for thermal energy Fe^+, Co^+, and Ni^+.[25] Beauchamp, however, has reported that Co^+ ions with greater than approximately 1 eV of kinetic energy will react with cyclopropane to produce $CoCH_2^+$ (reaction 20).[26]



(19)

I



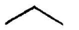
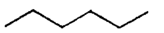
(20)

The reaction of V^+ with cyclobutane produces mainly $VC_2H_4^+$ by loss of ethene, while some dehydrogenation, producing $VC_4H_6^+$, is also seen. The $VC_2H_4^+$ produced probably results from insertion into one of the strained C–C bonds, resulting in formation of a vanadacyclopentane ion, II. Analogous metallacyclic ions have been proposed for the groups 8–10 metal ions, Fe^+, Co^+, and Ni^+.[17,25] In solution phase chemistry, metallacyclopentane species are observed to undergo thermal decomposition with loss of C_2H_4, β-hydride transfer to produce butene, and reductive elimination of cyclobutane.[27] The vanadacyclopentane ion can readily ring open to a bis(ethylene) structure (reaction 21), which eliminates C_2H_4 to produce $VC_2H_4^+$. The reverse reaction apparently does not occur since no $VC_4H_6^+$ is observed when ethene reacts with $VC_2H_4^+$. A similar result was also reported for the groups 8–10 transition metal ions.[17] The $VC_4H_6^+$ ion can be explained as arising from a β-hydride transfer in the metallacycle II to produce a butene complex which subsequently eliminates H_2. $VC_2H_4^+$ will undergo further reaction with cyclobutane producing, by dehydrogenation, $VC_6H_{10}^+$ and $VC_6H_6^+$. Formation of a $VC_4H_6^+$ species is also a secondary reaction of V^+–ethylene, as well as formation of the bis(ethylene)vanadium ion. The structure of the latter ion was confirmed by CID.

(21)

II

Table IV. Primary Product Distributions for the Reactions of VO^+ with Linear Alkanes

alkane	neutral(s) lost	relative %
CH_4	no reaction	
C_2H_6	no reaction	
	no reaction	
	H_2	100
	H_2	95
	CH_4, H_2	5
	$2H_2$	79
	C_2H_6, H_2	21

The $VC_4H_6^+$ ion also undergoes secondary reactions with cyclobutane, producing $VC_6H_6^+$ (shown to be a V^+–benzene ion by CID), $VC_8H_{10}^+$, and $VC_7H_8^+$.

Cyclopentane reacts with V^+ to produce a $VC_5H_6^+$ complex via loss of $2H_2$ as the only product. Formation of this product implies $D°(V^+–C_5H_6) > 50$ kcal mol^{-1}. This species undergoes a subsequent reaction with cyclopentane to produce, by loss of $3H_2$, $VC_{10}H_{10}^+$. This ion has a bis(cyclopentadienyl) structure as supported by CID in which the only products seen correspond to loss of C_5H_5 and, at high energy, reformation of the bare metal ion. Similar chemistry has been observed for the groups 8–10 metal ions.[17]

Cyclohexane provides continuing evidence that V^+ tends to induce dehydrogenation in organic species, showing two primary products, $VC_6H_8^+$ and V(benzene)$^+$. Formation of these products implies $D°(V^+–C_6H_8) > 55$ kcal mol^{-1} and $D°(V^+–C_6H_6) > 49$ kcal mol^{-1}. The $VC_6H_8^+$ complex undergoes a slow dehydrogenation to form the V(benzene)$^+$ complex, which reacts with cyclohexane to produce two products, $VC_{12}H_{14}^+$ and V^+–bis(benzene). While unusual, the apparent "spontaneous" dehydrogenation of $VC_6H_8^+$ to $VC_6H_6^+$ is not unprecedented.[20] Conversion from 1,3-cyclohexadiene to benzene is calculated to be ca. 6 kcal mol^{-1} exothermic,[12] and the conversion on the metal ion implies a low activation barrier for the reaction.

V^+ reacts with methylcyclohexane to produce $VC_7H_8^+$ and also $VC_6H_6^+$ as is the case for the groups 8–10 metal ions.[25] These products react with methylcyclohexane to produce, via two and three dehydrogenations, the expected bis(cycloalkapolyene) species.[25]

Reactions of VO^+ with Alkanes. In the solution chemistry of vanadium, numerous complexes of the vanadyl ion, VO^{2+},[28] have been prepared. Likewise, in the gas phase, VO^+ is a common product from the reaction of V^+ with molecular oxygen as well as with many oxygen-containing compounds. V^+ reacts rapidly with O_2, with a rate constant of ca. 6×10^{-10} cm^3 molecule^{-1} s^{-1}. This value is comparable to that reported by Staley and Kappes[29] and is approximately the Langevan rate, showing that reaction proceeds on nearly every collision. In the Staley and Kappes study, the general reaction 22 was investigated with several oxides of

$$V^+ + YO \rightarrow VO^+ + Y \qquad (22)$$

varying values of $D°(Y–O)$. By assuming that the occurrence of reaction 22 implies $D°(V^+–O) > D°(Y–O)$ and the converse, upper and lower limits for $D°(V^+–O)$ were established as $119 < D°(V^+–O) < 151$ kcal mol^{-1}. This is in excellent agreement with a recent report by Aristov and Armentrout of $D°(V^+–O) = 131 \pm 5$ kcal mol^{-1}.[3d]

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Table V. Primary Product Distributions for the Reactions of VO^+ with Branched Alkanes

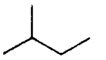
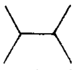
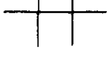
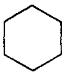
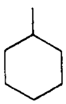
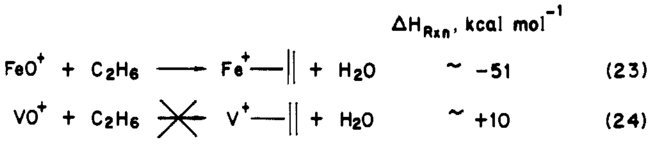
alkane	neutral(s) lost	relative %
	H_2	100
	H_2 $2H_2$ CH_4, H_2	39 42 19
	CH_4	100
	CH_4, H_2 $2H_2$	70 30
	C_4H_8 C_2H_6, $2H_2$ $3H_2$ $2H_2$ H_2	78 9 8 4 1

Table VI. Primary Product Distributions for the Reactions of VO^+ with Cyclic Alkanes

alkane	neutral(s) lost	relative %
	no reaction	
	C_2H_4	100
	$2H_2$ H_2	75 25
	$2H_2$ $3H_2$ H_2	70 19 11
	$3H_2$ CH_4, $2H_2$ $2H_2$ H_2	38 30 24 8

Since VO^+ forms rapidly when V^+ is generated in the presence of O_2, formation of VO^+ via pulsed valve addition of O_2 to trapped V^+ ions is a facile process. The VO^+ can then be isolated by swept double resonance ejection pulses and allowed to react with the hydrocarbon of interest, which is present at a low background pressure. Tables IV–VI list the primary reaction product distributions for the reactions of VO^+ with simple alkanes. In general, these reactions are slower than the reactions of the bare metal ion and, surprisingly, the presence of the oxide ligand does not significantly alter the observed chemistry. This is in marked contrast to an earlier study wherein the gas-phase reactions of FeO^+ with hydrocarbons were studied.[4] In that study, the presence of the oxide ligand was shown to increase the reactivity of the Fe^+, and exothermic water loss was postulated to account for the increased reactivity. This exothermicity can be attributed to the weaker Fe^+–O bond ($D°(Fe^+–O) = \sim 68$ kcal mol^{-1}; $D°(V^+–O) = \sim 131$ kcal mol^{-1}),[1c,3d] and the thermochemistry is compared in eq 23 and 24.[30] Thus, formation of the metal–olefin complex


ΔH_{Rxn}, kcal mol^{-1}

$$FeO^+ + C_2H_6 \longrightarrow Fe^+\text{—}\| + H_2O \quad \sim -51 \qquad (23)$$

$$VO^+ + C_2H_6 \not\longrightarrow V^+\text{—}\| + H_2O \quad \sim +10 \qquad (24)$$

with loss of water, as postulated for Fe^+, is not energetically favorable for V^+, and this reaction pathway is not seen. Formation of VO^+ from V^+ and O_2 is calculated to be 12 ± 5 kcal mol^{-1} exothermic.[3d,12] This low exothermicity, coupled with formation in the high-pressure O_2 pulse, suggests that all of the VO^+ formed is in the ground state. Nonetheless, the product distributions reported may be influenced by reactions involving a small fraction of the VO^+ ions containing some excess energy.

While the general reaction pathways for VO^+ with alkanes appear to be similar to those for V^+, there are differences in the extent of reaction, and in some cases, the absence of certain products indicates that VO^+ does not activate hydrocarbons to the same extent as does V^+.

Linear Alkanes. As was the case for V^+, VO^+ does not react with either methane or ethane. V^+ was observed, however, to undergo a slow reaction with propane, and this reaction is not seen with VO^+. With *n*-butane, V^+ induces both single and, predominantly, double dehydrogenation while VO^+ induces only a single dehydrogenation. Low-energy collisional activation of the VO^+–butene complex causes H_2 loss and high-energy CID regenerates VO^+, indicating that the structure of this ion is a VO^+–butene complex and not an aquo-V^+–butadiene complex. One would expect to see H_2O loss as a CID product if the complex were an aquo-V^+–butadiene species.[4] Formation of a VO^+–butene complex that converts to VO^+–butadiene upon low-energy collisional activation, along with the absence of direct VO^+–butadiene formation, again suggests that the VO^+ formed in the initial reaction with O_2 retains little excess internal energy, since excess energy would drive the VO^+–butene complex to form VO^+–butadiene. With pentane, also, the major product corresponds to a single H_2 loss with a small amount of VO^+–butadiene also formed. Hexane reacts with VO^+ to give analogous products corresponding to the major products of the reaction of V^+ with hexane, i.e., $VOC_6H_{10}^+$ via loss of $2H_2$ and $VOC_4H_6^+$ via loss of H_2 and C_2H_6.

Interestingly, secondary reactions are observed only for butane and not for pentane and hexane. Butane is observed to generate $VOC_8H_{14}^+$ via loss of $2H_2$ from $VOC_4H_8^+$ and butane. The absence of secondary reactions with the larger linear alkanes may imply that the primary product ion formed is coordinatively crowded, preventing any further reaction with the alkane.

Branched Alkanes. With branched alkanes, the chemistry of VO^+ becomes more interesting, with greater differences from the chemistry of V^+ observed. Isobutane is observed to react by loss of H_2 solely and does not, as it did with V^+, undergo a double dehydrogenation. CID of $VOC_4H_8^+$ shows that this ion has the VO^+–isobutene structure, since dehydrogenation to form $VOC_4H_6^+$, the CID product seen for linear butenes, is not observed. $VOC_4H_8^+$ reacts further to produce what is presumably a bis(methallyl)VO^+ complex via loss of $2H_2$. CID of this latter ion creates a number of products corresponding to dehydrogenations and loss of small hydrocarbons to form stable metal–olefin complexes, notably VO^+–benzene. All of these losses are analogous to CID of bis(methallyl)M^+ (M = V(vide supra), Fe, and Co[18]).

2-Methylbutane, on the other hand, shows in addition to the $2H_2$ loss product observed with V^+, products corresponding to loss of H_2 ($VOC_5H_{10}^+$) and $H_2 + CH_4$ ($VOC_4H_6^+$). Both of these ions yield VO^+ upon collisional activation. Neopentane shows the same primary reaction, loss of CH_4, with both V^+ and VO^+, but only one secondary product is observed with VO^+ as opposed to the several seen with V^+. This again suggests that coordinative saturation may occur sooner for VO^+ than V^+. VO^+ reacts with 2,3-dimethylbutane to produce one less product than is seen in the V^+ reaction. $VOC_5H_8^+$ and $VOC_6H_{10}^+$ are both formed, but the product presumably formed from insertion into the central C–C bond by V^+, $VC_3H_6^+$, does not have a corresponding product with VO^+. In contrast, the predominant product in the reaction of VO^+ with 2,2,3,3-tetramethylbutane is $VOC_4H_8^+$, presumably resulting from insertion into the central C–C bond of the molecule. Again, this bond is one of the weakest C–C bonds known,[23] and this fact presumably facilitates insertion.

Cyclic Alkanes. With cyclic alkanes, the reduced dehydrogenating power of VO^+ is once again exemplified. While V^+ reacts with cyclopropane (vide supra), VO^+ does not. With cyclobutane the only primary reaction product formed is, by loss of C_2H_4, $VOC_2H_4^+$. V^+, in comparison, produces $VC_2H_4^+$ and $VC_4H_6^+$

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(30) Calculated with use of values in ref 1c, 12, 23, and 4.

as primary reaction products. VOC$_2$H$_4^+$ then reacts rapidly to form VOC$_4$H$_6^+$ and VOC$_4$H$_8^+$. The VOC$_4$H$_6^+$ ion has a VO$^+$–butadiene structure, while the VOC$_4$H$_8^+$ ion is a bis(ethene) species, as is shown by the CID spectra of the two species. VOC$_4$H$_6^+$ regenerates VO$^+$ as the primary CID product, while VOC$_4$H$_8^+$ produces predominately VOC$_2$H$_4^+$ at low CID energies and VO$^+$ at high energies. With cyclopentane, both single and double dehydrogenations are seen with VO$^+$, while V$^+$ produces only the double dehydrogenation product. The product ions formed with VO$^+$ do react further to form VOC$_{10}$H$_{12}^+$, the bis(cyclopentadiene) product, and only a trace of VOC$_{10}$H$_{10}^+$, while the V$^+$ products react to produce exclusively the bis(cyclopentadienyl) product. Cyclohexane undergoes one, two, and three dehydrogenations with VO$^+$, while V$^+$ induces a minimum of two. Finally, VO$^+$ produces, again, products corresponding to one, two, and three dehydrogenations with methylcyclohexane, in addition to formation of VOC$_6$H$_6^+$, while V$^+$ forms only VC$_7$H$_8^+$ and VC$_6$H$_6^+$. None of the product ions from VO$^+$ react further with cyclohexane or methylcyclohexane, while secondary reactions are observed with V$^+$, again suggesting that the presence of the oxygen ligand reduces the number of coordination sites, preventing further interactions.

Conclusions

The V$^+$ ion reacts with hydrocarbons primarily by insertion into C–H bonds inducing dehydrogenation. In contrast to some of the later first-row transition-metal ions, such as Fe$^+$, Co$^+$, and Ni$^+$,[2b] formation of secondary reaction products occurs with all of the hydrocarbons studied save for the largest linear alkanes.

Addition of an oxide ligand to V$^+$, producing VO$^+$, does not greatly change the chemistry observed. VO$^+$ does react somewhat slower than V$^+$ and is not as effective at dehydrogenating alkanes. In cases where coordinative saturation may influence reactivity, such as formation of secondary products, an effect is seen. In contrast to FeO$^+$,[4] the oxide ligand does not appear to be involved in the reactions of VO$^+$, since it is never lost in the course of reaction, and collision-induced dissociation of product ions containing VO$^+$ always results in reformation of VO$^+$ by loss of other ligands. This effect is undoubtedly due to the strong V$^+$–O bond.

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Registry No. VO$^+$, 12192-26-6; V$^+$, 14782-33-3; CH$_4$, 74-82-8; C$_2$H$_6$, 74-84-0; propane, 74-98-6; butane, 106-97-8; pentane, 109-66-0; hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; nonane, 111-84-2; 2-methylpropane, 75-28-5; 2-methylbutane, 78-78-4; 2,2-dimethylpropane, 463-82-1; 2,3-dimethylbutane, 79-29-8; 2,2-dimethylbutane, 75-83-2; 2,2,3,3-tetramethylbutane, 594-82-1; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2.

Reactive Ion Pairs from the Charge-Transfer Excitation of Electron Donor–Acceptor Complexes

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Abstract: Excitation within the charge-transfer (CT) band of the electron donor–acceptor or EDA complexes of tetranitromethane (TNM) with a series of 9-substituted and 9,10-disubstituted anthracenes (An) leads to photochemistry in high quantum yields ($\Phi \sim 1$). The combined use of time-resolved picosecond spectroscopy, product isolation, and structure elucidation allows for the detailed mapping of the temporal evolution of the CT excited state to the photoproduct I via a series of discrete reactive intermediates. Thus electron transfer within the EDA complex occurs effectively (<25 ps) upon CT photoexcitation to form simultaneously An$^{+\cdot}$ and TNM$^{-\cdot}$. The latter is not observed directly owing to its spontaneous fragmentation to C(NO$_2$)$_3^-$ and NO$_2$ within 10 ps. The geminate ionic intermediates An$^{+\cdot}$ and C(NO$_2$)$_3^-$ undergo cage combination to produce hydranthryl radicals II within an interval of <500 ps. Photoproduct I derives from the encounter of the hydranthryl radical II with NO$_2$ subsequent to diffusive separation, consistent with the longer time scale of >1 ns and the trans stereochemistry required for the free radical coupling to occur. This detailed study is the basis for a generalized formulation (summarized in Scheme I) to be developed for CT photochemistry via reactive ion pairs. In particular, the comparison with the related EDA complexes of the anthracenes and tetracyanoethylene serves to emphasize the importance of back electron transfer from the geminate ion pair, i.e., $[D^{+\cdot}, A^{-\cdot}] \rightarrow [D, A]$.

Electron donor–acceptor or EDA complexes are commonly found as intermediates in a wide variety of reactions involving electron-rich species or donors (D), such as nucleophiles and bases, and electron-deficient acceptors (A).[2] For example, the well-known electrophilic aromatic substitutions such as chlorination, bromination, mercuration, thallation, etc., involve the EDA complexes of arenes with the acceptors Cl$_2$, Br$_2$, Hg(II), and Tl(III), respectively.[3] Since charge-transfer (CT) interactions provide substantial stabilization of the transition states for such processes,[4] we have begun a thorough picosecond spectroscopic study of the photochemical behavior of the excited states of EDA complexes.[5]

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